

THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAKIS-(CYANOMERCURI)METHANE HYDRATE

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Summary

The crystal structure of tetrakis(cyanomercuri)methane hydrate, $C(HgCN)_4 \cdot H_2O$, has been determined from diffractometer X-ray intensity data by means of Patterson and Fourier methods and refined by the least-squares technique based on 911 independent reflections to the index R of 0.058 and R_w of 0.065. Crystals are monoclinic holohedral, space group $P2_1/n$ with Z 4 formula units in the unit cell of dimensions a 8.520(5), b 13.622(8), c 10.783(6) Å, β 92.48(5)°, D_{obs} 4.99 g cm⁻³, D_{calc} 4.97 g cm⁻³. The structure consists of discrete molecules of tetrakis(cyanomercuri)methane and molecules of water of crystallization. The bond angles at the methane carbon atom range from 105(2) to 114(3)° and the mean Hg—C(methane) bond length is 2.05(3) Å, while the distance of all the four mercury atoms from the geometrical centre of the tetrahedron is 2.053(3) Å. The C—Hg—C bond angles range from 175(3) to 178(2)°. The mean value of the Hg—C(cyanide) bond length is 2.03 Å. The one O—H...N hydrogen bond per water molecule is 2.77 Å long.

Introduction

It has been shown recently [1] that Hofmann's mercarbide [2], originally thought to be a derivative of permercurated ethane and formulated as $C_2Hg_6O_2(OH)_2$, is actually a derivative of permercurated methane. Thus, as previously suggested [1], we call it Hofmann's base, instead of "ethane hexamer-carbide". Results obtained in our laboratory [3] showed Hofmann's base to have a polymeric structure, expressed by the formula $[CHg_4O(OH)_2]_n$. Unfortunately, it has not been possible so far to grow the crystals of the base to a size suitable for X-ray analysis, and so we have not been able to confirm the proposed formula.

Acids act on Hofmann's base either by forming salts (the salts of Hofmann's base) in which the structure of the polymeric $[CHg_4O]_n^{2n+}$ cation seems to be preserved, as shown previously by anion exchange experiments [2b], or by split-

TABLE 1
 ATOMIC COORDINATES AND THERMAL PARAMETERS σ , WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg(1)	0.5890(3)	0.2503(2)	0.1758(3)	114(3)	62(2)	105(3)	29(4)	-15(5)	-17(4)
Hg(2)	0.5937(4)	0.4911(2)	0.1773(3)	216(5)	66(2)	115(3)	-75(5)	-97(7)	26(5)
Hg(3)	0.2635(2)	0.3738(6)	0.2582(3)	78(3)	77(2)	168(3)	24(5)	-55(4)	-64(5)
Hg(4)	0.15949(3)	0.3702(2)	0.4452(3)	118(3)	52(1)	101(2)	11(4)	-32(4)	-5(5)

Atom	x/a	y/b	z/c	B (\AA^2)	Atom	x/a	y/b	z/c	B (\AA^2)
O(H ₂ O)	0.761(16)	0.380(12)	0.976(12)	20.5(39)	C(2)	0.668(8)	0.612(11)	0.089(7)	6.8(20)
N(1)	0.746(8)	0.073(6)	0.052(7)	7.4(17)	C(3)	0.024(11)	0.375(11)	0.267(8)	9.1(22)
N(2)	0.744(15)	0.688(8)	0.036(11)	13.4(35)	C(4)	0.683(5)	0.371(9)	0.622(4)	3.1(8)
N(3)	0.872(15)	0.376(12)	0.258(11)	15.1(32)	C(5)	0.502(4)	0.375(5)	0.261(4)	2.2(7)
N(4)	0.731(8)	0.368(8)	0.719(6)	7.0(14)					
C(1)	0.683(8)	0.131(11)	0.090(7)	6.3(17)	C _t	0.5047	0.3710	0.2655	

σ Anisotropic thermal parameters ($\times 10^4$) in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

ting the cation into tetrakis(anionomercuri)methane units of the $C(HgX)_4$ type. In our view, Hofmann's base, $[CHg_4O(OH)_2]_n$, should be considered as a condensation product of the unknown tetrakis(hydroxomercuri)methane, $C(HgOH)_4$. Thus, there are two distinct groups of permercurated methane derivatives: (i) Hofmann's base and its salts, e.g., the nitrate, $[CHg_4O]_n^{2n+}(NO_3)_{2n}$, and (ii) tetrakis(anionomercuri)methanes, e.g., the acetoxy or trifluoroacetoxy derivative, $C(HgOCOCH_3)_4$ or $C(HgOCOCF_3)_4$, as well as the other derivatives which we will describe in a separate paper. The cyanide, which belongs to the second group, was made as the monohydrate, $C(HgCN)_4 \cdot H_2O$, from the acetate by metathesis with potassium cyanide. Like the acetate and the trifluoroacetate [1], it forms well developed crystals; the availability of suitable crystals has so far limited our crystal structure determinations to only these three permercurated methane derivatives. The polymeric nature of the $[CHg_4O]_n^{2n+}$ cation is the reason why the salts of Hofmann's base have been obtained only in micro-crystalline form. However, we do not exclude the possibility of growing suitably large single crystals of the base and its salts under special conditions.

Experimental

Preparation. An aqueous solution of potassium cyanide (1.0 g in 15 ml) was added to the solution of tetrakis(acetoxymercuri)methane (3.0 g of Hofmann's base in 60 ml of 2 M acetic acid). The white precipitate was recrystallized from acetone, dried, and analyzed. Found: C, 6.47; H, 0.31; Hg, 85.64. $C_5H_2Hg_4N_4O$ calcd.: C, 6.41; H, 0.22; Hg, 85.68%. Loss of weight on drying (110°C); found 1.88, calcd. for the monohydrate: 1.92%.

Slow evaporation of the acetone solution gave crystals of two different forms, needle-shaped and prismatic, in approximately equal amounts. The needle-shaped crystals are not stable, and become white and disintegrate into a white powder. A solution in acetone of either of these two forms separated mechanically, again gives the mixture of both forms, proving that they are crystal modifications of a single compound. The chemical analysis are also identical.

The crystal structure determination has been carried out only on the stable prismatic form.

Infrared data (cm^{-1}): 3550m, 3440m, 2170m, 2030 (sh), 1620s, 723s, 670s (br) (Nujol mull, on Perkin-Elmer infrared grating spectrophotometer Model 337).

Crystal data. $C_5H_2N_4OHg_4$, mol. wt. 936.46, monoclinic, a 8.520(5), b 13.622(8), c 10.783(6) Å, β 92.48(5)°, V 1250.3 Å³, D_{obs} 4.99 gcm^{-3} , D_{calc} 4.97 gcm^{-3} , Z 4, space group $P2_1/n$ (No. 14), $F(000)$ 1552, Mo- K_α radiation, λ 0.7107 Å, $\mu(Mo-K_\alpha)$ 499 cm^{-1} .

Intensity measurements. The integrated intensities of 1229 reflections from a specimen ground to a sphere ($2R = 0.26$ mm) were collected within the interval of $2^\circ < \theta < 30^\circ$ on a computer controlled automatic diffractometer Philips PW 1100 (graphite monochromatized Mo- K_α radiation, $\omega - 2\theta$ scan technique, scan range 1.5° , scan rate $0.05^\circ s^{-1}$). Intensities of three standard reflections 103, 301 and 080, each measured over 120 minutes, showed steady linear weakening up to 8% at the end of the collection. The specimen darkened but remained transparent. The 911 independent reflections with $I > 3\sigma(I)$ were used in the struc-

ture analysis. Corrections for absorption, Lorentz, polarization and decay effects were applied.

Determination and refinement of the structure. The structure was solved by means of a three-dimensional Fourier synthesis based upon the mercury atom coordinates obtained from the Patterson synthesis. After a preliminary refinement of light-atom positions by means of a difference synthesis, the structure was refined by full matrix least-squares method assigning anisotropic temperature factors to the mercury atoms only. The final values of the reliability indices R and R_w , $\{R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$ were 0.058 and 0.065, with $w = 1/\sigma^2(F_o)$. The assignment of anisotropic temperature factors also to the light atoms did not improve the agreement; the R values did not change significantly, but some of the temperature factors took on unusual values. The high value of the isotropic B factor of 20.4 \AA^2 for the water oxygen atom is explained by a loose packing of the water molecule (see Description of the structure). The atomic scattering factors were those of Cromer and Mann [4] with corrections for the real and imaginary parts of the anomalous dispersion for the mercury atom only [5]. The final values of atomic coordinates and thermal parameters are listed in Table 1. A list of observed and calculated structure factors can be obtained from the authors on request. Calculations were carried out on the UNIVAC 1110 of the SRCE, University Computing Centre, Zagreb, using the programmes described in ref. [6].

Description of the structure

The crystal structure of tetrakis(cyanomercuri)methane hydrate consists of discrete $C(HgCN)_4$ molecules and water molecules as shown in Fig. 1. Since the distance of 2.77 \AA between the water oxygen and the N(4) nitrogen atoms is a comparatively short intermolecular contact, the hydrate as a whole must be considered the structural entity. The contact refers to the $O-H \cdots N$ hydrogen bond [7]; as evidenced by its length and by the infrared spectra (see Experimental).

The tetrahedron of four mercury atoms around the carbon atom dominates the structure and has the dominant influence on the intensity of reflections. Since the coordinates of the mercury atoms are determinable to the highest accuracy (see Table 1), the geometry of the mercury atom tetrahedron is the most precisely known part of the structure. The tetrahedron edges, given separately in Table 3, have been determined with a mean e.s.d. of 0.004 \AA . The departure from the ideal tetrahedron is best seen from the $Hg-C-Hg$ bond angle values, which lie within the range 105 to 114° (Table 2). The $Hg \cdots Hg$ tetrahedron edges, which are geometrically determined only by the covalent $Hg-C(5)$ bond length and the $Hg-C(5)-Hg$ bond angles, are larger than the Van der Waals distances, which are expected to be about 3.0 \AA [8,9], but less than the second $Hg \cdots Hg$ distance of 3.466 \AA in solid metallic mercury [10].

The values of light-atom coordinates, as obtained from the least-squares refinement, are considerably less accurate (Table 1) because of the dominating influence of the mercury atom on the majority of the medium and strong reflections. Thus, only a few such reflections can bias the light-atom coordinates in the least-squares calculation. This is particularly true for the central carbon atom,

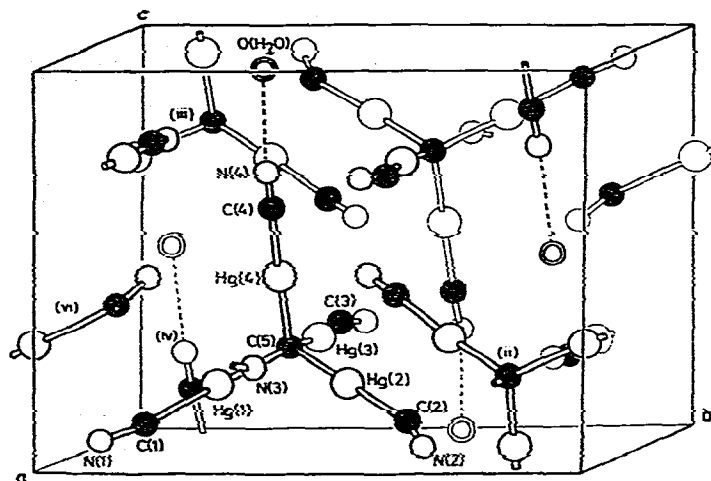


Fig. 1. A perspective view of the crystal structure (the unit cell) of tetrakis(cyanomercuri)methane hydrate.

C(5), surrounded by four mercury atoms at covalent bond distance which is expected to be about 2.05 Å [8]. The refinement gave four different values for these distances from 2.00 to 2.11 Å (Table 2). In the structure of the analogous trifluoroacetoxy derivative [1], where the position of the central carbon atom is determined by the space group symmetry (at the inversion tetrad) all four Hg—C bonds are defined by only one distance value, for which the refinement gave 2.042(4) Å. In the present structure the position of the central carbon atom is not fixed by symmetry and consequently is very sensitive to the accuracy of the observed structure amplitudes. There is no reason for the C(5) carbon atom to be off the centre of the mercury tetrahedron, since all the four mercury

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°), WITH STANDARD DEVIATIONS IN PARENTHESES ^a

Distances		Distances		Angles	
C(5)—Hg(1)	2.08(6)	Hg(1)—N(3)	3.05(15)	Hg(1)—C(5)—Hg(2)	107(2)
C(5)—Hg(2)	2.00(6)	Hg(1)—O(H ₂ O) ⁱ	3.19(14)	Hg(1)—C(5)—Hg(3)	111(3)
C(5)—Hg(3)	2.03(4)	Hg(2)—N(3)	2.95(15)	Hg(1)—C(5)—Hg(4)	105(2)
C(5)—Hg(4)	2.11(4)	Hg(2)—O(H ₂ O) ⁱ	3.05(15)	Hg(2)—C(5)—Hg(3)	114(3)
Hg(1)—C(1)	2.05(12)	Hg(2)—N(1 ⁱⁱ)	3.36(7)	Hg(2)—C(5)—Hg(4)	108(2)
Hg(2)—C(2)	2.02(12)	Hg(3)—N(2 ^v)	3.23(12)	Hg(3)—C(5)—Hg(4)	110(2)
Hg(3)—C(3)	2.05(10)	Hg(3)—N(1 ⁱⁱⁱ)	3.26(7)	C(5)—Hg(1)—C(1)	178(3)
Hg(4)—C(4)	2.02(5)	Hg(3)—N(4 ^{iv})	3.34(11)	C(5)—Hg(2)—C(2)	175(3)
C(1)—N(1)	1.05(14)	Hg(4)—N(1 ⁱⁱ)	3.07(7)	C(5)—Hg(3)—C(3)	177(3)
C(2)—N(2)	1.17(17)	Hg(4)—N(2 ^{vi})	3.08(12)	C(5)—Hg(4)—C(4)	178(2)
C(3)—N(3)	1.29(16)	Hg(4)—N(3)	3.17(12)	Hg(1)—C(1)—N(1)	172(9)
C(4)—N(4)	1.11(8)	Hg(4)—N(1 ⁱⁱⁱ)	3.33(7)	Hg(2)—C(2)—N(2)	163(10)
O(H ₂ O)—N(4)	2.77(15)			Hg(3)—C(3)—N(3)	173(10)
O(H ₂ O)—N(3)	3.15(17)			Hg(4)—C(4)—N(4)	178(6)

^a Transformation of the asymmetric unit (x,y,z): (i) x,y,z - 1; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (v) 1 - x, 1 - y, -z; (vi) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

TABLE 3

THE LENGTHS OF THE Hg...Hg TETRAHEDRON EDGES IN Å, WITH THE e.s.d. IN PARENTHESES

H(1)...Hg(2)	3.280(4)	Hg(2)...Hg(3)	3.382(5)
Hg(1)...Hg(3)	3.394(5)	Hg(2)...Hg(4)	3.325(4)
Hg(1)...Hg(4)	3.332(4)	Hg(3)...Hg(4)	3.398(3)

atoms are chemically equivalent whereas the differences in the intermolecular contacts are too small to be of any significant influence on the Hg—C(5) bond lengths. Thus we suggest the possibility that the geometrical centre of the mercury tetrahedron, C_t , i.e., the centre of the sphere defined by the coordinates of Hg(1), Hg(2), Hg(3) and Hg(4), is the true position of the methane carbone atom, and the distance from C_t to any of four mercury atoms in the tetrahedron is the true Hg—C bond length in this structure. From the coordinates of the tetrahedron centre (Table 1), calculated by formulae of solid analytic geometry, and the mercury atom coordinates, a value of 2.053(3) Å was derived for the Hg—C distance. This is very close to the value of 2.05 Å, the mean of four Hg—C(5) distances obtained from the least squares refinement (Table 2). The Hg— C_t bond length is in a very good agreement with previously determined Hg—C bond lengths [11], and is close to the sum of the corresponding covalent radii [8,12].

The Hg—C(cyanide) distances of 2.05, 2.02, 2.05 and 2.02 Å, at Hg(1), Hg(2), Hg(3) and Hg(4), respectively, with a mean value of 2.03 Å, agree well with the Hg—C(cyanide) distance of 2.05(1) Å in methylmercury(II) cyanide determined by neutron diffraction [13], but is less than the Hg—C(cyanide) value of 2.094(16) Å found in phenylmercury(II) cyanide by X-ray diffraction [14]. The value of 2.015(3) Å for the Hg—C distance in mercury(II) cyanide was obtained by neutron diffraction [15]. The C—N bond length values of 1.05, 1.17 and 1.11 Å for C(1)—N(1), C(2)—N(2) and C(4)—N(4), respectively, are in fairly good agreement with the value of 1.14(1) Å found in methylmercury(II) cyanide [13]. The larger value of 1.29 Å for C(3)—N(3) can be explained by the interaction of the N(3) nitrogen atom with three mercury atoms, Hg(1), Hg(2) and Hg(4), of the neighbouring molecule which, in a way, belongs to the coordination sphere of all these three mercury atoms. The packing of the cyanide molecules appears to be favoured by hydration. The close juxtaposition of the HgCN groups of the neighbouring molecules leaves one hole per molecule, and this is occupied by the water molecule (see Fig. 1). The closest water—oxygen to cyanide—nitrogen contact of 2.77 Å agrees with the value of 2.883(5) Å for the O—H...N hydrogen bond determined unambiguously by neutron diffraction in tetraaquobis[dicyanomercurey(II)]zinc(II) nitrate trihydrate [16]. The remaining Hg(1)...O and Hg(2)...O contacts of 3.19 and 3.05 Å, respectively, as well as the N(3)...O contact of 3.15 Å, are not as close, but the position of the other water hydrogen atom must be taken into account in their interpretation. The values of all other intermolecular distances are as expected from the conventional van der Waals radii, taken as about 1.50 Å for mercury [8,9]. The Hg...N distances from 2.95 to 3.36 Å are anisometric, as previously observed by Bondi [17], i.e., they are larger in the direction normal to the C—N bond.

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